

Claims:

1. A biocompatible tissue-bonding adhesive composition comprising:  
a polyol of functionality N, wherein said polyol being terminated with at least one polyisocyanate in solution with at least (N-1)% of said solution comprising free polyisocyanate.
2. The biocompatible composition as recited in claim 1 wherein N is in the range 1.5 – 8.
3. The biocompatible composition as recited in claim 1 wherein said polyol is a branched polypropylene/polyethylene oxide copolymer.
4. The biocompatible composition as recited in claim 3 wherein said polypropylene/polyethylene oxide copolymer contains polypropylene oxide in a range of about 10% and 30%.
5. The biocompatible composition as recited in claim 3 wherein said polypropylene/polyethylene oxide copolymer contains no more than 10% polypropylene oxide.

6. The biocompatible composition as recited in claim 1 wherein said polyisocyanate is comprised of a 80:20 mixture of 2,4-toluene diisocyanate and 2,6-toluene diisocyanate.
7. The biocompatible composition as recited in claim 1 wherein said polyisocyanate consists of 2,6-toluene diisocyanate.
8. The biocompatible composition as recited in claim 1 wherein said polyisocyanate consists of isophorone diisocyanate.
9. The biocompatible composition as recited in claim 1 wherein said polyisocyanate consists of an 80:20 mixture of 2,4-toluene diisocyanate and 2,6-toluene diisocyanate and 3% of the composition is free polyisocyanate.
10. The biocompatible composition as recited in claim 1 wherein said polyisocyanate consists of isophorone diisocyanate and about 1.5% of said composition consists of free polyisocyanate.

11. The biocompatible composition as recited in claim 1, wherein said composition is comprised of two polyisocyanates and wherein one of said polyisocyanates comprises a free isocyanate B as an aromatic polyisocyanate and the other of said polyisocyanates comprises an aliphatic isocyanate A which is used to endcap said copolymer.
12. The biocompatible composition as recited in claim 11 wherein the free isocyanate B converts to an amine faster than the isocyanate A.
13. The biocompatible composition as recited in claim 11 wherein said free isocyanate B is more reactive with nitrogenous substances than said isocyanate A.
14. The biocompatible composition as recited in claim 11 wherein said free isocyanate B is of lower viscosity than said isocyanate A.
15. A biocompatible adhesive composition comprising of at least two branched polyols of functionality 1.5-8, said polyols being terminated with at least one polyisocyanate in solution

- with at least 1% of said solution comprising free polyisocyanate.
16. The biocompatible composition as recited in claim 15 wherein at least one of said polyols is a branched polypropylene/polyethylene oxide copolymer.
  17. The biocompatible composition as recited in claim 16 wherein one of said branched polyols consists of a copolymer of less than 10% polypropylene oxide and another of said branched polyols comprises a copolymer consisting of between 10 and 30% polypropylene oxide, both of said copolymers of functionality 1.5-8, said copolymers being terminated with at least one polyisocyanate in solution with at least 1% of said solution comprising free polyisocyanate.
  18. The biocompatible composition as recited in claim 17 wherein one of said polyol copolymers consists of 5% polypropylene oxide and the other of said polyol copolymers consists of 25% polypropylene oxide.
  19. The biocompatible composition as recited in claim 17 wherein said copolymer having a lesser functionality

comprises at least 25% by molecular number of the total copolymer component.

20. The biocompatible composition as recited in claim 15 wherein one of said copolymers has functionality less than the other of said copolymers.
21. The biocompatible composition as recited in claim 20 wherein one of said copolymers has functionality 2 and the other of said copolymers has functionality 3.
22. The biocompatible composition as recited in claim 20 wherein said copolymer of lesser functionality is less than 25% by molecular number of the total copolymer component.
23. The biocompatible composition as recited in claim 22, wherein one polyol is terminated with a polyisocyanate with water reactivity R1 and another polyol is terminated with a polyisocyanate with water reactivity R2, where  $R1 > R2$ , both of said terminated polyols of functionality 1.5-8, said terminated polyols being in solution with at least 1% of said solution comprising free polyisocyanate of reactivity R1.

24. The biocompatible composition as recited in claim 23 wherein one of said polyols is terminated with an aromatic polyisocyanate and another of said polyols is terminated with an aliphatic polyisocyanate, both of said polyols of functionality 1.5-8, said terminated polymers in solution with at least 1% of said solution comprising free polyisocyanate.
25. The biocompatible composition as recited in claim 24 wherein said free polyisocyanate is aromatic.
26. The biocompatible composition as recited in claim 25, wherein said free polyisocyanate is comprised of toluene diisocyanate.
27. The biocompatible composition as recited in claim 25, wherein said free polyisocyanate consists of isomer 2,6-toluene diisocyanate.
28. The biocompatible composition as recited in claim 23, wherein said composition eliminates amines during polymerization induced by water or proteins where said less reactive isocyanate capped polyol is present in stoichiometric amounts.

29. The biocompatible composition as recited in claim 28, wherein said isocyanate used to cap said polyol comprises isophorone diisocyanate.
30. The biocompatible composition as recited in claim 29, wherein said polyol is 75% polyethylene oxide and 25% polypropylene oxide.
31. A method for covalent bonding of tissue, which comprises:  
applying to said tissue a 1-part surgical adhesive consisting essentially of at least one NCO-terminated branched polymer, derived from at least one organic polyisocyanate and at least 1% unreacted polyisocyanate wherein the polymerization proceeds by the following time-ordered steps:  
1) free polyisocyanate bonds to tissue,  
2) said free polyisocyanate converts to a polyamine and links said NCO-terminated branched polymer to said tissue bonded polyisocyanate;

- 3) said free polyisocyanate converts to polyamine and links said branched polymer to other said same polymers.
32. The method for the covalent bonding of tissue as recited in claim 31 wherein said polymer comprises a polypropylene/polyethylene copolymer.
33. A method for covalent bonding of tissue, which comprises:
- applying to said tissue a 1-part surgical adhesive consisting essentially of a NCO-terminated branched polymer, derived from an organic polyisocyanate A and at least 1% unreacted polyisocyanate B wherein polyisocyanate B is more reactive with amine groups than polyisocyanate A and wherein the polymerization proceeds by the following time-ordered steps:
- 1) polyisocyanate B bonds to tissue,
  - 2) said free polyisocyanate B converts to a polyamine and links said polyisocyanate A-terminated branched polymer to said tissue bonded polyisocyanate B,

- 3) said free polyisocyanate B converts to polyamine and links said branched polymer to other said same polymers.
34. The method of claim 33 wherein said polymer comprises a polypropylene/polyethylene copolymer.
35. A method for covalent bonding of tissue, which comprises:  
applying thereto a 1-part surgical adhesive consisting essentially of a NCO-terminated branched polymer, derived from an aromatic polyisocyanate A and at least 1% unreacted polyisocyanate A and a NCO-terminated branched polymer, derived from an aliphatic polyisocyanate B, wherein the polymerization proceeds by the following time-ordered steps:  
1) polyisocyanate A bonds to tissue,  
2) 2) said free polyisocyanate A converts to a polyamine and links said polyisocyanate A-terminated branched polymer to said tissue bonded polyisocyanate A,  
3) said free polyisocyanate A converts to polyamine and links said polyisocyanate A terminated branched polymers to other said

polyisocyanate A terminated branched polymers, 4) said free polyisocyanate A converts to polyamine and links to polyisocyanate B terminated branched polymers.

36. The method as recited in claim 35 comprising the additional step 5 of:

converting said free polyisocyanate A to polyamine; and linking polyisocyanate B terminated branch polymers to other NCO terminated branched polymers.

37. The method as recited in claim 35 wherein said polymer is a copolymer of polyethylene oxide and polypropylene oxide.
38. A method for covalent bonding of tissue, which comprises:

applying thereto a 1-part surgical adhesive consisting of two NCO-terminated branched polypropylene/polyethylene oxide copolymers, wherein copolymer A is at most 10% polypropylene oxide and copolymer B is between 10% and 30% polypropylene oxide, derived from an organic polyisocyanate and at least 1% unreacted polyisocyanate

wherein the polymerization proceeds by the following time-ordered steps:

- 1) free polyisocyanate bonds to tissue,
- 2) said free polyisocyanate converts to a polyamine and links both polypropylene/polyethylene oxide copolymers to said tissue bonded polyisocyanate,
- 3) said free polyisocyanate converts to polyamine and links said branched polypropylene/polyethylene oxide copolymers to other said same polymers, and
- 4) polymerized copolymer A swells within the formed polymer matrix and causes degradation of the formed matrix.

39. A method for covalent bonding of tissue, which comprises:

applying thereto a 1-part surgical adhesive consisting of two NCO-terminated branched polypropylene/polyethylene oxide copolymers, wherein copolymer A is at most 10% polypropylene oxide and copolymer B is between 10% and 30% polypropylene oxide, wherein copolymer A is

substantially more viscous than copolymer B, derived from an organic polyisocyanate and at least 1% unreacted polyisocyanate wherein the polymerization proceeds by the following time-ordered steps:

- 1) free polyisocyanate bonds to tissue,
- 2) said free polyisocyanate converts to a polyamine and links copolymer B preferentially to said tissue bonded polyisocyanate,
- 3) said free polyisocyanate converts to polyamine and links said branched polypropylene/polyethylene oxide copolymers to other said same polymers,
- 4) polymerized copolymer A swells within the formed polymer matrix and causes degradation of the formed matrix, and
- 5) polymerized copolymer B does not swell at the tissue/matrix interface and does not cause tissue bond degradation.